Indian J. Phys. **68B** (6), 549 – 555 (1994)

IJP B
- an international journal

Ultrasonic relaxation in some organic liquids and their activation energies

A V Narasimham and B Manikiam*
Department of Physics, Indian Institute of Technology, Madras 600 036, India

Received 11 March 1994, accepted 19 July 1994

Abstract : The concept of the complex and frequency dependent bulk viscosity coefficient of a liquid is used to obtain expressions for the ultrasonic relaxation time in terms of absorption and dispersion of the wave in the liquid. Available experimental data on ultrasonic absorption and dispersion are used to calculate the ultrasonic relaxation times in nine liquids at various temperatures Variation of relaxation time with temperature is used to calculate activation energies for these liquids. It is found that the orders of magnitude of relaxation times and values of activation energies are fairly reasonable

Keywords : Ultrasonic relaxation, activation energies, organic liquids .

PACS Nos. : 43.35 Bf, 43.35. Fj, 62.60 + v

Propagation of low intensity ultrasonic waves and measurement of their absorption and dispersion in liquids form an important method for the evaluation of various thermodynamic and inter and intra-molecular processes in liquids. Absorption and dispersion can be connected to the inter [1,2] and intra [3,4] molecular relaxation times. The response of the medium, under the action of an ultrasonic wave, is not exactly in phase with the applied pressure wave, due to inertia of the molecules (or atoms) and various intermolecular (or atomic) forces operating in the medium, leading to a phase shift between cause and effect. This phase shift leads to an intermolecular (*e.g.* compressional) relaxation in the liquid, leading to absorption and dispersion of the wave in the liquid. A part of the energy of the wave is utilised to excite internal modes (rotational, vibrational *etc.*) leading to intramolecular relaxation. This paper discusses evaluation of intermolecular ultrasonic relaxation times (τ) using the concept of the bulk viscosity [1] coefficient of a liquid. The temperature variations of relaxation times are used to evaluate the molecular activation energies (U).

*Now in India Meteorological Department, New Delhi-110 003, India

The complex (*) and frequency (ω) dependent bulk viscosity coefficient (η_b^*) [1] of a liquid is closely connected [2] with ultrasonic absorption [5], dispersion and relaxation [1] by the following equations :

$$\eta_b^* = \eta_1(\omega) - i\,\eta_2(\omega), \tag{1}$$

$$\eta_1(\omega) - \eta_1(\infty) = [\eta_1(0) - \eta_1(\infty)]\,[1/(1 + \omega^2\tau^2), \tag{1a}$$

and

$$\eta_2(\omega) = [\eta_1(0) - \eta_1(\infty)]\,[\omega\tau/(1 + \omega^2\tau^2), \tag{1b}$$

$\eta_1(0)$ and $\eta_1(\infty)$ are the values of the in-phase component $\eta_1(\omega)$, at very low and very high frequencies. ω is the angular frequency of the ultrasonic wave, propagated through the liquid; τ is the bulk viscous relaxation time, associated with dilatational processes in the liquid. τ is connected with the transition of the molecules from one equilibrium position to another, due to compressional viscosity of the medium. We also have the following equations

$$(\alpha/\omega^2) = [\eta_1(\omega) + (4/3)\,\eta_s)/2\,\rho V_0^3, \tag{2a}$$

and

$$2\rho\,V_0(V - V_0) = \omega\,\eta_2(\omega), \tag{2b}$$

where α is the amplitude absorption coefficient of the wave, η_s is the shear viscosity coefficient of the liquid, ρ is the density of undisturbed liquid, V_0 is the wave velocity at very low frequencies, V is the velocity at any frequency ω, and $\eta_2(\omega)$ is the imaginary component of $\eta_b^*(\omega)$. For liquids that are considered in the present context, $\eta_1(\omega) \gg \eta_s$. Hence, η_s can be neglected in eq. (2a) without much error. Also, $\eta_1(\omega)$ decreases with ω, according to eqs. (1a) and (2a). Hence, $\eta_1(\infty) \gg \eta_1(\omega) < \eta_1(0)$. Making these approximations, we get from eqs. (1) and (2)

$$\tau \simeq (1/\omega)\left[\{\eta_1(0) - \eta_1(\omega)\}/\eta_1(\omega)\right]^{1/2}. \tag{3a}$$

Combining eqs. (2a) and (3a), we also set

$$\tau \simeq (1/\omega)\left[\{(\alpha/\omega^2)_{l.f} - (\alpha/\omega^2)_{u.f}\}/(\alpha/\omega^2)_{u.f}\right]^{1/2}, \tag{3b}$$

where *l.f* and *u.f* refer to low and ultrasonic frequencies. We also have, according to eqs. (1b) and (2b)

$$[\omega\,\eta_2(\omega)] = [\{\eta_1(0) - \eta_1(\infty)\}/\tau]\,[\omega^2\tau^2/(1 + \omega^2\tau^2)], \tag{4a}$$

or

$$[\omega\,\eta_2(\omega)]_{\omega\to\infty} = [\eta_1(0) - \eta_1(\infty)]/\tau \simeq \eta_1(0)/\tau, \tag{4b}$$

and also

$$[\omega\,\eta_2(\omega)]_{\omega\to\infty} = 2\,\rho V_0(V_\infty - V_0). \tag{5}$$

But according to eq. (2a), we also have

$$\eta_1(0) \simeq 2\,\rho V_0^3\,(\alpha/\omega^2)_{l.f} \tag{6}$$

Combining eqs. (4), (5) and (6), we get for τ,

$$\tau = [V_0^2/(V_\infty - V_0)]\,(\alpha/\omega^2)_{l.f} \tag{7}$$

From eqs. (1) and (2), using the aforesaid approximations,we get

$$\omega\tau \simeq \eta_2(\omega)/\eta_1(\omega) \simeq (V - V_0)/[V_0^2(\alpha/\omega)], \tag{8}$$

or $$\tau = (V - V_0)/[\omega^2(\alpha/\omega^2)_{u.f} V_0^2]. \tag{9}$$

Using eqs. (1b), (2b), (4) and (5), we also get

$$\tau = (1/\omega)[(V - V_0)/(V_\infty - V)]^{1/2}. \tag{10}$$

Eqs. (3b), (7), (9) and (10) give various expressions for ultrasonic relaxation time (τ) due to bulk viscosity of the medium. We also have

$$\tau = \tau_0 \exp(U/kT), \tag{11}$$

where τ_0 is a constant (independent of temperature, T), U is the molecular activation energy, associated with transition of molecules from one equilibrium position to the next, k is Boltzman's constant and T is in degrees Kelvin. A plot of log τ *vs* $1/T^0A$ gives τ_0 and U.

Experimental data required for these calculations are obtained from literature [6–17]. All the data required for the aforesaid eqs. (3b), (7), (9) and (10) are not available neatly in all the references. For example eq. (3b) requires ω, $(\alpha/\omega^2)_{l.f}$ and $(\alpha/\omega^2)_{u.f}$ at the same frequency, but at various temperatures for evaluation of τ at these temperatures and hence U.

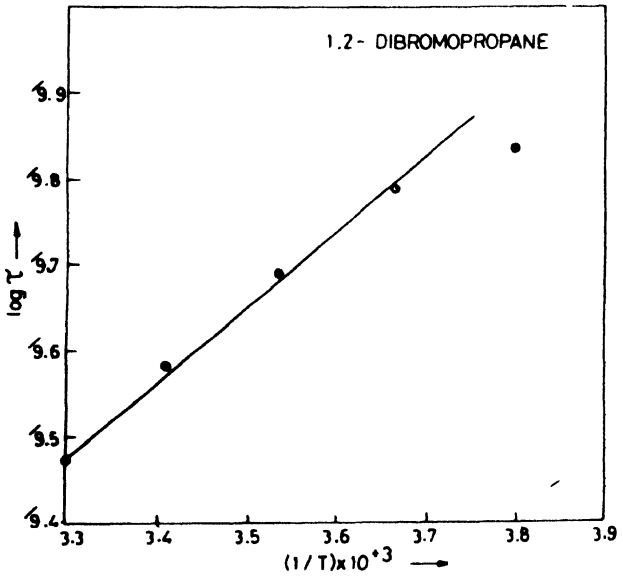

Figure 1. Variation of log τ with $1/T°$ A for 1,2-dibromopropane.

Different workers [6–17] have presented their experimental data at slightly different frequencies, at various temperatures. Thus, the values of $(\alpha/\omega^2)_{l.f}$ and $(\alpha/\omega^2)_{u.f.}$ at various temperatures used in the present calculations, refer to slightly different frequencies, and not (strictly) at a single frequency. This may result in a very negligible error in the values of τ and

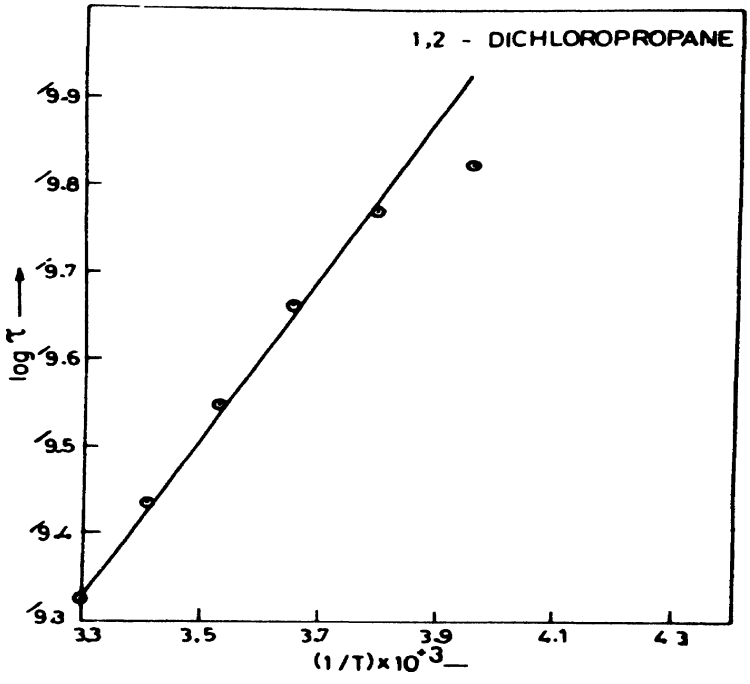

Figure 2. Variation of log τ with $1/T$ ° A for 1,2-dichloropropane

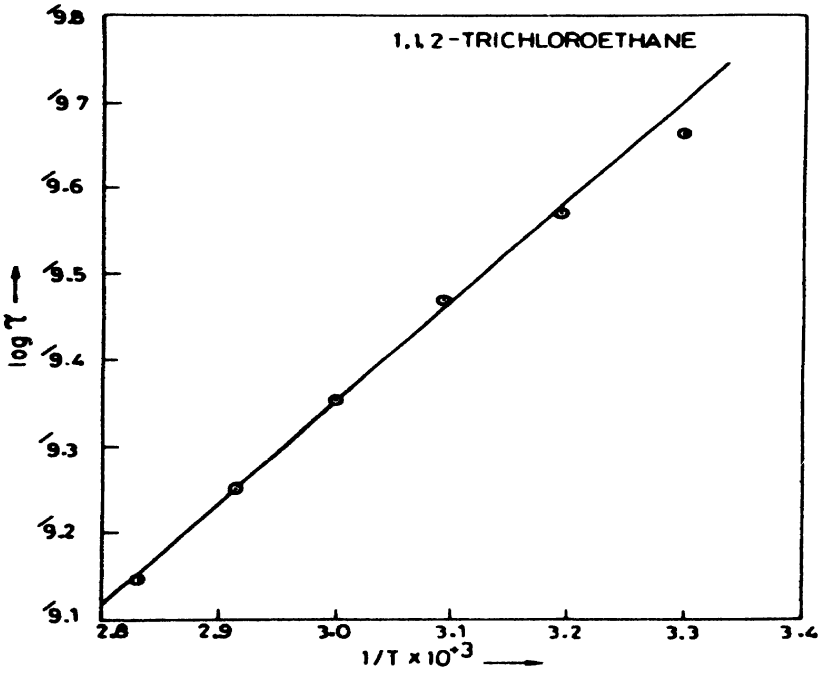

Figure 3. Variation of log τ with $1/T$ ° A for 1,1,2-trichloroethane.

practically no error in U. Experimental data required for these calculations are chosen from the data, reported by various [6–17] authors. Hence, these data are not reproduced here. Likewise, V_0, V_∞ and $(\alpha/\omega^2)_{l.f}$ required for evaluation of τ at various temperatures, are obtained by suitable extrapolation of the existing data [6–17] on the frequency scale. These

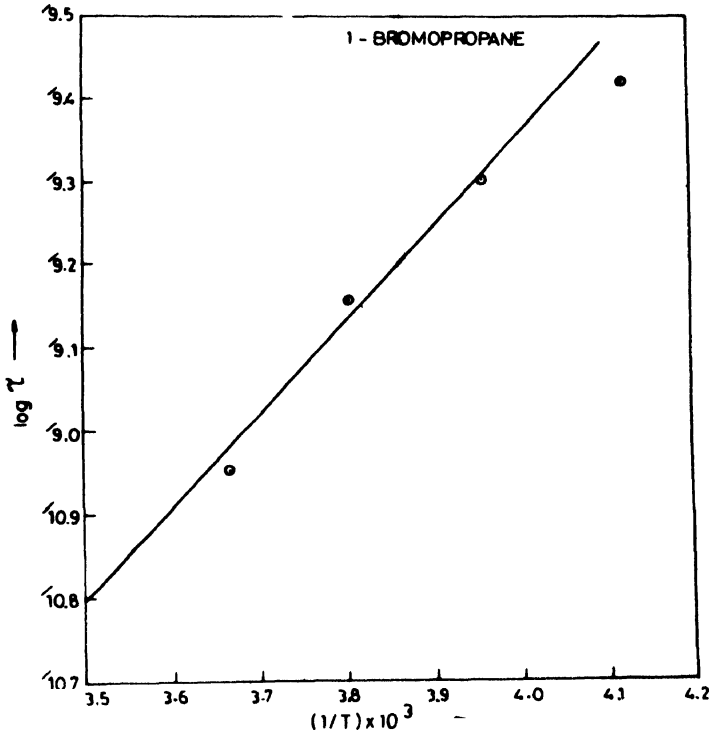

Figure 4. Variation of log τ with $1/T$ ° A for 1-bromopropane.

extrapolations are not shown here. Values of ω, $(\alpha/\omega^2)_{u.f}$ and V, for the various calculations refer to ultrasonic frequencies, between 5 to 15 MHz (even more in some cases), at various temperatures. Thus, the relaxation times are calculated for nine liquids, using one (or other) of the four eqs. (3b), (7), (9) and (10), making a suitable choice of the equation, according to available data, at various temperatures. These values are given in Figures 1 to 4 (and hence, no table is presented for the variation of τ with T), for four liquids. The circled dots (⊙) are the experimental points, in Figures 1 to 4. In addition, similar calculations are made, and similar plots between $\log\tau$ and $1/T^0A$ are drawn, in the case of five more liquids, shown in Table 1, which gives the values of τ, τ_0 and U for all the nine liquids.

It may be noted from Table 1, that the order of magnitude of the relaxation times in these associated liquids is fairly large. Acetic acid has the largest relaxation time. It may be reasonable to have relatively large values for τ, in associated liquids which exhibit relatively high ultrasonic absorption (and hence large relaxation time). The activation energies (U) are small (about 0.1 to 0.3 eV), consistent with known activation energies for many liquids. It may be noted that U depends upon the rate of change of τ with T and does not depend much

on the absolute value of τ. τ_0 gives the relaxation time at very high temperatures ($T \rightarrow \infty$ or $(1/T) \rightarrow 0$). Examination of Figures 1 to 4 shows some non-linearity in the variation of log τ *vs* $1/T$, at higher values of $1/T$, or lower temperatures. This may be, partly, due to the fact

Table 1. Values of activation energies and relaxation times using existing data and equations (3b), (7), (9) and (10).

	Liquid	τ in sec at 303^0A $\times 10^9$	τ_0 in sec	Activation energy (eV)
1.	1,2-dibromopropane	2.985	5.577×10^{-12}	0.1744
2.	1,2-dichloropropane	2.113	1.971×10^{-12}	0.1820
3.	1, 1,2-trichloroethane	4.677	7.584×10^{-13}	0.2315
4.	1-bromopropane	0.3715	4.563×10^{-15}	0.2778
5.	n-propyl alcohol	0.3278 (at 243°A)	6.673×10^{-12}	0.0898
6.	Pentachlorobiphenyl	9.797	5.136×10^{-13}	0.2381
7.	2-methyl pentanediol [2,4]	1.126	3.814×10^{-13}	0.1985
8.	Hexanetrial [1,2,6]	4.624	4.890×10^{-13}	0.2447
9.	Acetic Acid	54.12	1.325×10^{-10}	0.154

that shear viscosity (η_s) has been neglected in the above equations, and usually, η_s increases as temperature decreases. Thus, these equations may not be valid well at low temperatures. Possible error (slight) in experimental data may also lead to some experimental points away from the linear plot. However, more experimental points may be needed, to confirm the deviation from linear behaviour of the log τ *vs* $1/T$ plots.

In conclusion, it may be added that measurement of ultrasonic absorption and dispersion in liquids provides a very convenient way to study their molecular properties.

Acknowledgment

One of the authors (BM) wishes to thank the Council of Scientific and Industrial Research, India, for the award of a research scholarship to carry out this work.

References

[1] A V Narasimham, *IEEE Transactions on Sonics and Ultrasonics* **SU 16** p 182 (1969)

[2] L Hall *Phys. Rev.* **73** 775 (1948)

[3] L Tisza *Phys. Rev.* **61** 531 (1942)

[4] J M M Pinkerton *Proc. Phy. Soc. (London)* **B62** 129 (1949)

[5] K F Herzfeld and T A Litovitz *Absorption and Dispersion of Ultrasonic Waves* (New York : Academic) Ch. 1 (1959)

[6] J Karpovich *J: Chem. Phys.* **22** 1767 (1954)

[7] P Vigoureux *Ultrasonics* (New York : Wiley) p 129 (1951)

[8] A B Bhatia *Ultrasonic Absorption* (London : Oxford Univ. Press) p 171 (1967)

[9] D Sette *Phys. Rev.* **78** 476 (1950)

[10] C Eckart *Phys. Rev.* **73** 68 (1948)

[11] L N Liebermann *Phys. Rev.* **75** 1415 (1949)

[12] J Lamb and J M M Pinkerton *Proc. Roy. Soc. (London)* **A199** 114 (1949)

[13] R Meister *et al J. Appl. Phys.* **31** 854 (1960)

[14] T Lyon and T A Litovitz *J. Appl. Phys.* **27** 179 (1956)

[15] T A Litovitz, T Lyon and L Peselnick *J. Acoust. Soc. America* **26** 566 (1954)

[16] J Lamb *Z. Electrochem.* **64** 136 (1960)

[17] R A Padmanabhan *J. Sci. Indus. Res. (India)* **19** 336 (1959)